

**METHOD FOR REDUCING THE NITROGEN  
CONTENT OF PETROLEUM STREAMS WITH  
REDUCED SULFURIC ACID CONSUMPTION**

**FIELD OF THE INVENTION**

[0001] The instant invention relates to a method for upgrading nitrogen-containing hydrocarbon streams. More particularly, the present invention relates to a method for producing low-nitrogen hydrocarbon products involving contacting a hydrocarbon feedstream with an acidic solution to selectively remove heterocyclic nitrogen-containing compounds, recovering a used sulfuric acid solution, and cascading the used sulfuric acid solution to another contacting stage.

**BACKGROUND OF THE INVENTION**

[0002] Currently, there exists a need to reduce the sulfur and aromatics content of motor fuels, in particular diesel, to meet current environmental emission regulations. While both the sulfur and aromatics content of diesel boiling range feedstreams from which diesel motor fuels are derived can be reduced to a satisfactory level through the use of catalytic treatments, the catalytic treatments are severely impeded by nitrogen-containing compounds present in the feedstream. Thus, many methods for reducing the nitrogen content in feedstreams, such as those used in sulfur and aromatics reducing processes, for motor fuel production have been proposed.

[0003] For example, United States Patent Number 3,719,587 teaches the use of dilute sulfuric acid (0-10 wt%) to remove basic nitrogen species from coal liquifaction derived naphtha. Unfortunately, hydrotreating catalysts are not only poisoned by basic nitrogen species, but also by non-basic nitrogen heterocycles that are abundant in diesel boiling range feedstreams. For this

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reason, stronger sulfuric acid has been used to remove substantially all of the nitrogen species.

[0004] There also exists a need to reduce the heterocyclic nitrogen content of feedstreams used in the lube oil processes because heterocyclic nitrogen-containing compounds, especially basic heterocyclic nitrogen-containing compounds, contained in lube oil boiling range feedstreams act as competitive inhibitors on the catalytic sites of catalysts. These nitrogen-containing compounds are indigenous to crude oils, and are typically concentrated in the higher boiling fractions, such as lube oil fractions. The presence of these heterocyclic nitrogen-containing compounds typically prevents lube oil hydroprocesses from operating as effectively and/or efficiently as possible. For example, the presence of these heterocyclic nitrogen-containing compounds in lube oil boiling range feedstreams used in hydrocracking operations requires that the hydrocracking be performed at high temperatures that impart a higher degree of over-cracking and lube oil boiling range yield loss when compared to hydrocracking processes that operate at a lower temperature.

[0005] Also, the removal of nitrogen species from lube oil boiling range feedstreams allow cracking operations to operate more efficiently because these heterocyclic nitrogen-containing compounds, especially basic heterocyclic nitrogen-containing compounds, act as competitive inhibitors on the acidic cracking sites of cracking catalysts. Thus, many methods for reducing the nitrogen content in feedstreams have been proposed.

[0006] Also, United States Statutory Invention Registration H1368, Fraytet, teaches the use of concentrated sulfuric acid, i.e. at least 95 wt.% sulfuric acid,

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to treat straight run jet fuel boiling range streams. The process requires that the sulfuric acid-containing stream be dispersed in the jet fuel in the form of droplets smaller than about 300 microns. The Fraytet process discloses that 90% or more of the nitrogen can be removed from the jet fuel boiling range stream. However, as Fraytet points out, separation of the acid from the feedstream is critical to avoid unwanted secondary reactions from occurring, such as, for example, polymerization of olefins and reaction of sulfuric acid with thiophenic species. These unwanted reactions are detrimental in several ways. First the unwanted side reactions force the practitioner of these processes to utilize more sulfuric acid because these reactions consume a portion of the sulfuric acid. Secondly, it degrades the product by forming high-boiling polymers from olefinic materials, which become soot-formers in subsequent combustion. Finally, some of the byproducts from these unwanted reactions are removed due to solubility in the acid byproduct and lead to an overall yield loss for the process.

[0007] However, it is also known in the art that dispersive contacting methods such as those of Fraytet have certain drawbacks such as "pepper sludge" formation. Pepper sludge formation occurs when the tiny droplets of acid are not readily coalesced or settled in gravity settlers. The dispersed acidic material suspended in the feed is thus carried over with the treated feed, and practitioners of such processes are forced to utilize caustic treatments to neutralize the pepper sludge and avoid corrosion problems. However, the "pepper sludge" suspended in the feed also contains nitrogen species that were removed from the feed. Upon neutralization, the nitrogen species may be liberated and return to the feed. Thus, the existence of pepper sludge in dispersive treatment methods limits the ultimate level of nitrogen reduction that

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can be achieved. Therefore, there exists a need in the art for a more effective nitrogen removal method for diesel boiling range feedstreams.

[0008] Therefore, there still exists a need in the art for a more effective nitrogen removal method for hydrocarbon feedstreams which benefits the subsequent hydroprocessing of the hydrocarbon feedstreams, i.e. a process that more selectively removes nitrogen-containing heterocycles that poison hydroprocessing catalysts without incurring the debits listed above that are the result of unwanted chemistry.

#### **SUMMARY OF THE INVENTION**

[0009] The instant invention is directed at an improved hydroprocessing process for hydrocarbon feedstreams containing nitrogen contaminants. The process comprises:

- a) providing a sulfuric acid solution having a sulfuric acid concentration of at least about 75 wt.%, based on the sulfuric acid solution;
- b) contacting a first hydrocarbon feedstream containing nitrogen heteroatoms and having a Total Acid Number in a first contacting stage with the sulfuric acid solution under conditions effective at removing at least about 80 wt.% of the nitrogen heteroatoms contained in said hydrocarbon feedstream thereby producing at least a first stage effluent comprising at least a first hydrocarbon product stream and a first used sulfuric acid solution, wherein the volumetric treat rate of the sulfuric acid solution is greater than about 0.5 vol.%, based on the first hydrocarbon feedstream;
- c) separating said first used sulfuric acid solution and said first hydrocarbon product stream;

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- d) cascading at least a portion of said first used sulfuric acid solution to a second contacting stage;
- e) contacting a second hydrocarbon feedstream containing nitrogen heteroatoms and having a Total Acid Number in the second contacting stage with the first used sulfuric acid solution under conditions effective at removing at least about 80 wt.% of the nitrogen heteroatoms contained in said second hydrocarbon feedstream thereby producing at least a second stage effluent comprising at least a second hydrocarbon product stream and a second used sulfuric acid solution, wherein the volumetric treat rate of the first used sulfuric acid solution is greater than about 0.5 vol.%, based on the second hydrocarbon feedstream, wherein the concentration of nitrogen heteroatoms in said second hydrocarbon feedstream is higher than that of said first hydrocarbon feedstream;
- f) separating said second used sulfuric acid solution and said second hydrocarbon product stream; and
- g) contacting at least a portion of said first product stream with a hydroprocessing catalyst in a hydroprocessing reaction stage.

[0010] In one embodiment of the instant invention the sulfuric acid solution is a spent sulfuric acid solution obtained from an alkylation process unit wherein the spent sulfuric acid solution is produced by:

- a) combining an olefinic hydrocarbon feedstream containing C<sub>4</sub> olefins with isobutane to form a hydrocarbonaceous mixture; and
- b) contacting the hydrocarbonaceous mixture with sulfuric acid under conditions effective for producing at least an alkylate and a sulfuric acid solution having an acid concentration of at least about 75 wt.%.

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[0011] In another embodiment of the instant invention, at least a portion of the second hydrocarbon product stream is also contacted with a hydroprocessing catalyst in a hydroprocessing reaction stage.

[0012] In another embodiment of the instant invention the process further comprises separately contacting the first and second hydrocarbon product streams with an effective amount of an acid reducing material selected from caustic and water under conditions effective at reducing the total acid number of the hydrocarbon products prior to hydroprocessing.

[0013] In another preferred embodiment of the instant invention, the contacting of the first and second hydrocarbon product streams with the acid reducing material reduces the total acid number of the first and second hydrocarbon product streams to at least the total acid number of the first and second hydrocarbon feedstreams, respectively.

#### **DETAILED DESCRIPTION OF THE INSTANT INVENTION**

[0014] The instant invention is an improved hydroprocessing process involving removing nitrogen from hydrocarbon feedstreams containing both nitrogen and sulfur contaminants. The present invention involves contacting a hydrocarbon feedstream having a total acid number and containing both nitrogen and sulfur contaminants with a sulfuric acid solution thereby producing at least a first effluent comprising at least a first hydrocarbon product stream and a first used sulfuric acid solution, wherein the volumetric treat rate of the sulfuric acid solution is greater than about 0.5 vol.%, based on the first hydrocarbon feedstream. The first stage effluent is then separated into



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a first used sulfuric acid solution and a first hydrocarbon product stream. At least a portion of the first used sulfuric acid solution is cascaded to a second contacting stage. In the second contacting stage a second hydrocarbon feedstream containing nitrogen heteroatoms and having a Total Acid Number is contacted with the first used sulfuric acid solution under conditions effective at removing at least about 80 wt.% of the nitrogen heteroatoms contained in the second hydrocarbon feedstream. It should be noted that the concentration of nitrogen heteroatoms in the second hydrocarbon feedstream is higher than that of the first hydrocarbon feedstream. The second contacting stage produces a second effluent comprising at least a second hydrocarbon product stream and a second used sulfuric acid solution. The second stage effluent is then separated into a second used sulfuric acid solution and a second hydrocarbon product stream. At least a portion of the first product stream is then contacted with a hydroprocessing catalyst in a hydroprocessing reaction stage.

[0015] It should be noted that "hydrocarbon feedstream" as used herein is meant to refer to a hydrocarbon feedstream containing both nitrogen and sulfur contaminants and possessing a Total Acid Number ("TAN").

[0016] The first and second hydrocarbon feedstreams suitable for treatment in the present invention boil above 300°F and include those streams considered to boil within the distillate range through the lube oil range. As used herein, distillate boiling range includes streams boiling in the range of about 300°F to about 775°F, preferably about 350°F to about 750°F, more preferably about 400°F to about 700°F, most preferably about 450°F to about 650°F. These include distillate boiling range feedstreams that are not hydrotreated, are a blend of non-hydrotreated distillate boiling range feedstreams, previously

hydrotreated distillate boiling range feedstreams, blends of hydrotreated distillate boiling range feedstreams, and blends of non-hydrotreated and hydrotreated distillate boiling range feedstreams. The distillate boiling range feedstreams suitable for use herein can also contain greater than 10%, based on the distillate boiling range feedstream, of cracked stock. It should be noted that a hydrotreated distillate boiling range feedstream is to be considered a feedstream that has been contacted with an effective hydrotreating catalyst under effective hydrotreating conditions prior to being contacted with a sulfuric acid solution.

[0017] Distillate boiling range feedstreams as used herein typically have a nitrogen content as high as about 2500 wppm nitrogen, preferably about 50 to about 2500 wppm nitrogen, more preferably about 75 to about 1000 wppm nitrogen, and most preferably about 100 to about 750 wppm nitrogen. The nitrogen appears as both basic and non-basic nitrogen species. Non-limiting examples of basic nitrogen species may include quinolines and substituted quinolines, and non-limiting examples of non-basic nitrogen species may include carbazoles and substituted carbazoles. The sulfur content of such streams is typically about 40 wppm to about 35000 wppm sulfur, preferably about 250 wppm to about 35000 wt.% sulfur.

[0018] Lube oil boiling range feedstreams as used herein includes any conventional lube oil boiling range feedstreams used in lube oil processing. Such feedstreams typically include wax-containing feedstreams such as feeds derived from crude oils, shale oils and tar sands as well as synthetic feeds such as those derived from the Fischer-Tropsch process. Typical wax-containing feedstocks for the preparation of lubricating base oils have initial boiling points



of about 599°F (315° C) or higher. Non-limiting examples of lube oil boiling range feedstreams include feeds such as reduced crudes, hydrocrackates, extracts, hydrotreated oils, atmospheric gas oils, vacuum gas oils, coker gas oils, atmospheric and vacuum resids, deasphalted oils, slack waxes, raffinates, and Fischer-Tropsch wax. Such feeds may be derived from distillation towers (atmospheric and vacuum), hydrocrackers, hydrotreaters and solvent extraction units, and may have wax contents of up to 50% or more. Preferred lube oil boiling range feedstreams boil above about 650°F (343°C).

[0019] As mentioned above, raffinates are suitable for use in the present process. Lube oil boiling range raffinates are produced by solvent extracting a lube oil boiling range feedstream, such as those described above. In this embodiment, the lube oil raffinates so produced boil within the range described above and preferred lube oil boiling range raffinates boil above about 650°F (343°C). The lube oil boiling raffinate may also comprise mixtures of lube oil raffinates boiling within the above-defined parameters. Thus, more than one lube oil boiling range feedstream can be solvent extracted, and the resulting lube oil boiling range raffinates combined to form one lube oil boiling range raffinate that is contacted with the sulfuric acid solution. The lube oil raffinates may be either fully or partially extracted, i.e. under-extracted. By under-extracted it is meant that, the extraction is carried out under conditions such that the raffinate yield is maximized while still removing most of the lowest quality molecules from the feed. Raffinate yield may be maximized by controlling extraction conditions, for example, by lowering the solvent to oil treat ratio and/or decreasing the extraction temperature.

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[0020] Lube oil raffinates used herein can be produced under standard solvent extracting conditions, and the conditions chosen are not critical as long as the raffinate so produced meets the above-described boiling range criteria. Typically, the solvent extracting process involves contacting a lube oil boiling range stream with an extraction solvent. The extraction solvent can be any solvent known that has an affinity for aromatic hydrocarbons in preference to non-aromatic hydrocarbons. Non-limiting examples of such solvents include sulfolane, furfural, phenol, and N-methyl pyrrolidone ("NMP"). Furfural, phenol, and NMP are preferred.

[0021] The lube boiling range stream can be contacted with the extraction solvent by any suitable solvent extraction method. Non-limiting examples of such include batch, semi-batch, or continuous. It is preferred that the extraction process be a continuous process, and it is more preferred that the continuous process be operated in a counter-current fashion. In a counter-current configuration, it is preferred that the lube oil boiling range feedstream be introduced into the bottom of an elongated contacting zone or tower and caused to flow in an upward direction while the first extraction solvent is introduced at the top of the tower and allowed to flow in a downward direction, counter-current to the upflowing lube oil boiling range feedstream. In this configuration, the lube oil boiling range feedstream is forced to pass counter-currently to the extraction solvent resulting in the intimate contact between the extraction solvent and the lube oil boiling range feedstream. The extraction solvent and the light lube stream migrate to opposite ends of the contacting zone.

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[0022] The conditions under which the extraction solvent is contacted with the lube oil boiling range feedstream can be any conditions known to be effective in the solvent extraction of lube oil boiling range feedstreams. In a preferred embodiment, the temperature and pressure are selected to prevent complete miscibility of lube oil boiling range feedstream in the extraction solvent.

[0023] The contacting of the lube oil boiling range feedstream with the extraction solvent produces at least a first aromatics-rich extract solution and a first aromatics-lean raffinate solution. It should be noted that as used herein, aromatics-lean is meant to refer to the concentration of aromatics present in the raffinate phase produced by solvent extraction in relation to the concentration of aromatics present in the extract phase produced by solvent extraction. The first aromatics-lean raffinate solution is then treated to remove at least a portion of the extraction solvent contained therein, thus producing the lube oil boiling range raffinate that can be used herein. The removal of at least a portion of the extraction solvent can be done by any means known in the art effective at separating at least a portion of an extraction solvent from an aromatics lean raffinate solution. Preferably the lube oil boiling range raffinate is produced by separating at least a portion of the first extraction solvent from the first aromatics-rich extract solution in a stripping or distillation tower. By at least a portion, it is meant that at least about 80 vol%, preferably about 90 vol%, more preferably 95 vol%, based on the first aromatics-lean raffinate solution, of the extraction solvent is removed from the aromatics-lean raffinate solution. Most preferably substantially all of the extraction solvent is removed from the aromatics-lean raffinate solution. It should be noted that when the solvent

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extracting method that produces the lube oil boiling range raffinate is referenced herein, it is meant to encompass this separation step.

[0024] Lube oil boiling range feedstreams typically contain greater than about 100 wppm nitrogen, more typically the nitrogen concentration ranges from about 1000 wppm to about 2000 wppm. The nitrogen compounds appear as both basic and non-basic nitrogen species in the lube oil boiling range feedstreams. Again, non-limiting examples of basic nitrogen species may include quinolines and substituted quinolines, and non-limiting examples of non-basic nitrogen species may include carbazoles and substituted carbazoles.

[0025] In practicing the instant invention, a first hydrocarbon feedstream is intimately contacted with a sulfuric acid solution. The sulfuric acid solution used herein is suited for the composition of the hydrocarbon feedstream treated. However, typical acid solutions contain greater than about 75 wt.% sulfuric acid, based on the sulfuric acid solution, preferably greater than about 80 wt.%, and more preferably about 85 to about 93 wt.%. The sulfuric acid solution may be obtained through any means known. It is preferred that the sulfuric acid solution be the spent acid from an alkylation process unit having a sulfuric acid concentration within the above-defined ranges. A typical alkylation process involves combining an olefinic hydrocarbon feedstream containing C<sub>4</sub> olefins with isobutane to produce a hydrocarbonaceous mixture. This hydrocarbonaceous mixture is subsequently contacted with sulfuric acid. The sulfuric acid used for contacting the hydrocarbonaceous mixture is typically reagent grade sulfuric acid having an acid concentration of at least about 95 wt.%. Preferably the sulfuric acid has a sulfuric acid concentration of greater than about 97 wt.%. The hydrocarbonaceous mixture is contacted with the

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sulfuric acid under conditions effective at producing at least an alkylate and a spent sulfuric acid solution. The latter is sometimes referred to as "spent alkylation acid". The sulfuric acid solution so produced comprises at least about 75 wt.% sulfuric acid, based on the sulfuric acid solution, preferably greater than about 80 wt%, more preferably about 85 wt. % to about 92 wt%, about 0.5 to about 5 wt.% water, with the remaining balance being acid soluble hydrocarbons. It is more preferred that the effective conditions be selected such that the sulfuric acid solution so produced comprises between about 82 and 95 wt.% sulfuric acid, about 3 to about 10 wt % water, with the remaining balance being soluble hydrocarbons. However, it is most preferred that the effective conditions be selected such that the sulfuric acid solution so produced comprises between about 85 and 93 wt.% sulfuric acid, about 4 to about 8 wt.% water, with the remaining balance being soluble hydrocarbons.

[0026] As mentioned above, the concentration of sulfuric acid in the sulfuric acid solution is dependent on the type of stream treated. If the first hydrocarbon feedstream is a non-hydrotreated distillate or a blend of non-hydrotreated distillates, the sulfuric acid solution preferably has an acid concentration of greater than about 76 wt.%, a water concentration of about 2 wt.% to about 12 wt.%, and a dissolved oil concentration of less than about 12 wt.%; more preferably an acid concentration of about 85wt.% to about 89 wt.%, a water concentration of about 6 wt.% to about 10 wt.%, and a dissolved oil concentration of about 5 wt.% to about 9 wt.%. If the distillate stream is a hydrotreated distillate, or a blend of hydrotreated distillates, each of which may or may not contain cracked stock, the sulfuric acid solution preferably has an acid concentration of greater than about 79 wt.%, a water concentration of about 2 wt.% to about 9 wt.%, and a dissolved oil concentration of less than



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about 12 wt.%; more preferably an acid concentration of about 88 wt.% to about 93 wt.%, a water concentration of about 4 wt.% to about 6 wt.%, and a dissolved oil concentration of about 5 wt.% to about 10 wt.%. If the distillate stream is a non-hydrotreated distillate or a blend of distillates, containing greater than 10% cracked stock, based on the distillate or blend, the sulfuric acid solution preferably has an acid concentration of greater than about 79 wt.%, a water concentration of about 2 wt.% to about 9 wt.%, and a dissolved oil concentration of less than about 12 wt.%; more preferably an acid concentration of about 84 wt.% to about 91 wt.%, a water concentration of about 5 wt.% to about 10 wt.%, and a dissolved oil concentration of about 5 wt.% to about 12 wt.%.

[0027] If the first hydrocarbon feedstream is a lube oil boiling range feedstream, excluding raffinates, the sulfuric acid solution used herein contains at least about 75 wt.% sulfuric acid, based on the sulfuric acid solution, preferably greater than about 80 wt.%, more preferably about 85 wt.% to about 93 wt.%. Therefore, the spent alkylation acid produced from the alkylation process unit contains about 0.5 to about 5 wt.% water, with the remaining balance being acid suspended hydrocarbons. If the hydrocarbon feedstream is a lube oil boiling range feedstream, it is more preferred that the alkylation unit be run under effective conditions selected such that the sulfuric acid solution so produced comprises between about 82 and 92 wt.% sulfuric acid, about 1 to about 4 wt.% water, with the remaining balance being suspended hydrocarbons; however, it is most preferred that the effective conditions be selected such that the sulfuric acid solution so produced comprises between about 85 and 93 wt.% sulfuric acid, about 1.5 to about 4 wt.% water, with the remaining balance being suspended hydrocarbons.



[0028] If the first hydrocarbon feedstream is a raffinate, the sulfuric acid solution used contains at least about 75 wt.% sulfuric acid, based on the sulfuric acid solution, preferably greater than about 85 wt.%, more preferably about 92 wt.% to about 98 wt.%. If the sulfuric solution is spent sulfuric acid, the alkylation process unit is run under conditions effective at producing a sulfuric acid solution comprising at least about 75 wt.% sulfuric acid, based on the sulfuric acid solution, preferably greater than about 80 wt.% sulfuric acid, more preferably about 80 vol.% to about 95 wt.% sulfuric acid. Again, the sulfuric acid solution also typically contains about 0.5 to about 5 wt.% water, with the remaining balance being acid suspended hydrocarbons. It is more preferred that the effective conditions be selected such that the sulfuric acid solution so produced comprises between about 82 and 92 wt.% sulfuric acid, about 1 to about 4 wt.% water, with the remaining balance being suspended hydrocarbons. However, it is most preferred that when the first hydrocarbon feedstream is a raffinate that the effective conditions of the alkylation process unit be selected such that the sulfuric acid solution so produced comprises between about 92 and 98 wt.% sulfuric acid, about 1.5 to about 4 wt.% water, with the remaining balance being suspended hydrocarbons.

[0029] It should be noted that it is within the scope of the present invention to dilute the sulfuric acid solution obtained from the alkylation unit, or otherwise, with a suitable diluent, preferably water, in order to provide a sulfuric acid solution having the above-described concentration of sulfuric acid, i.e. greater than about 75 wt.% sulfuric acid, etc. In order to determine the sulfuric acid concentration once the diluent has been added to the sulfuric acid solution, the sulfuric acid content and water content are measured by standard

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analytical techniques. The equivalent acid strength can then be calculated with the following formula:  $\text{equivalent wt\% sulfuric acid} = \text{wt\% sulfuric acid} / (\text{wt\% sulfuric acid} + \text{wt\% water})$ . In this formula, the acid soluble hydrocarbon content of the spent alkylation acid is treated as an inert diluent with respect to the sulfuric acid and water content.

[0030] The first hydrocarbon feedstream is contacted with the sulfuric acid solution in a first contacting stage. The treat rate of the sulfuric acid solution in the contacting stages used herein is also dependent on the type of hydrocarbon feedstream used. Distillate boiling range and lube oil boiling range feedstreams are contacted with the sulfuric acid solution at an acid volumetric treat rate of greater than about 0.5 vol.%, based on the distillate boiling range feedstream, preferably about 1 to about 10 vol.%, and more preferably 1 to about 6 vol.%. If the distillate boiling range feedstream contains greater than about 40 wt.% cracked stock, then the most preferred treat rates are about 2 vol.% to about 6 vol.%, based on the distillate boiling range feedstream. Raffinates are contacted with the sulfuric acid solution at an acid volumetric treat rate of greater than about 0.1 vol.%, based on the lube oil boiling range raffinate, preferably greater than about 0.5 vol.% more preferably about 0.5 vol.% to about 2.0 vol.%.

[0031] The contacting of the hydrocarbon feedstream and the sulfuric acid solution in the first contacting stage can be achieved by any suitable method including both dispersive and non-dispersive methods. Non-limiting examples of suitable dispersive methods include mixing valves, mixing tanks or vessels, and other similar devices. Non-limiting examples of non-dispersive methods include packed beds of inert particles and fiber film contactors such as those

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sold by Merichem Company and described in United States Patent Number 3,758,404, which is hereby incorporated by reference, which involve contacting along a bundle of metallic fibers rather than a packed bed of inert particles. Preferred contacting methods are non-dispersive, and more preferred contacting methods are those that are classified as dispersive.

[0032] The contacting of the hydrocarbon feedstream with the sulfuric acid solution in the first contacting stage occurs under effective conditions. Effective conditions are also dependent on the type of hydrocarbon feedstream used. If the hydrocarbon feedstream is a distillate boiling range feedstream or a raffinate, effective conditions are to be considered those conditions that allow for a reduction of the nitrogen content of the distillate boiling range feedstream by greater than about 80 wt.%, preferably greater than about 85 wt.% more preferably greater than about 90 wt.%. Effective conditions are also to be considered those conditions that minimize yield losses during the sulfuric acid solution treatment to about 0.5 to about 6 wt.%, preferably about 0.5 to about 4 wt.%, and more preferably about 0.5 to about 3 wt.%. If the hydrocarbon feedstream is a lube oil boiling range feedstream, excluding raffinates, effective conditions are to be considered those conditions that allow the present method to achieve a reduction of nitrogen of at least about 60 wt.%, preferably greater than about 75 wt.%, more preferably greater than 80 wt.%.

[0033] The contacting of the first hydrocarbon feedstream with the sulfuric acid solution in the first contacting stage produces a first stage effluent comprising at least a first hydrocarbon product stream and a first used sulfuric acid solution. The first used sulfuric acid solution, which now contains the removed nitrogen species, is then separated from the first hydrocarbon product

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stream. The first used sulfuric acid solution and the first hydrocarbon product stream can be separated by any means known to be effective at separating an acid from a hydrocarbon stream. Non-limiting examples of suitable separation methods include gravity settling, electric field induced settling, centrifugation, microwave induced settling and settling enhanced with coalescing surfaces. However, it is preferred that the first hydrocarbon product stream and the first used sulfuric acid solution be separated, or allowed to separate, into layers in a separation device such as a settling tank or drum, coalescer, electrostatic precipitator, or other similar device. In one embodiment, the above-described fiber-film contactors can be used for separating the first used sulfuric acid solution and the first hydrocarbon product stream. The first hydrocarbon product stream is withdrawn from the separation device and conducted to a suitable hydroprocessing process.

[0034] After the first used sulfuric acid solution and the first hydrocarbon product have been separated, the first used sulfuric acid solution is cascaded to a second contacting stage. It is preferred that the first used sulfuric acid solution have an acid concentration within the ranges discussed above. For example, if the second hydrocarbon feedstream is a distillate boiling range feedstream, it is preferred that the first used sulfuric acid solution have an acid concentration within the ranges discussed above for distillate boiling range feedstreams.

[0035] In the second contacting stage, a second hydrocarbon feedstream is contacted with the first used sulfuric acid solution. The second hydrocarbon feedstream can be any of those described above. However, the second hydrocarbon feedstream is a higher nitrogen content feedstream than the first

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hydrocarbon feedstream. Preferably the nitrogen level of the second hydrocarbon feedstream is about 100 % to about 1000 % higher than that of the first hydrocarbon feedstream.

[0036] The second hydrocarbon feedstream is contacted with the first used sulfuric acid solution under effective conditions. Effective conditions are to be considered any of those discussed above in reference to the first contacting stage, and are also dependent on the make-up of the second hydrocarbon feedstream. For example, if the second hydrocarbon feedstream is a distillate boiling range feedstream, effective conditions are to be considered those effective conditions discussed above in relation to distillate boiling range feedstreams.

[0037] The contacting of the second hydrocarbon feedstream with the sulfuric acid solution in the second contacting stage produces a second stage effluent comprising at least a second hydrocarbon product stream and a second used sulfuric acid solution. The second used sulfuric acid solution, which now contains the removed nitrogen species, is then separated from the second hydrocarbon product stream. The second used sulfuric acid solution and the second hydrocarbon product stream can be separated by any means discussed above in relation to the first hydrocarbon product stream and first sulfuric acid solution.

[0038] As discussed above, the first hydrocarbon product stream is conducted to a suitable hydroprocessing process. Hydroprocessing, as used herein, is meant to refer to any catalytic process using hydrogen treat gas in the presence of a hydroprocessing catalyst designed to facilitate the desired



reaction. Non-limiting examples of suitable hydroprocessing processes include hydrotreating, hydrocracking, ring opening, aromatics saturation, hydrodewaxing, and hydrofinishing. It should be noted that the hydroprocessing process should be selected according to the desired reaction and the make-up of the first hydrocarbon product stream. It should also be noted that if the first hydrocarbon product stream results from a lube oil boiling range feedstream, this product stream can also be conducted to a solvent dewaxing process.

[0039] In one embodiment of the instant invention, the second hydrocarbon product stream is also conducted to a suitable hydroprocessing process. Suitable hydroprocessing processes are those discussed above, and if the second hydrocarbon product stream results from a lube oil boiling range feedstream, this product stream can also be conducted to a solvent dewaxing process.

[0040] The sulfuric acid treatment of the first and second hydrocarbon feedstreams discussed above, however, also results in hydrocarbon product streams that are typically more acidic than the hydrocarbon feedstream used in the production of the hydrocarbon product stream. For example, the first hydrocarbon product stream is typically more acidic than the first hydrocarbon product stream. The measure of acidity referenced herein is the total acid number ("TAN") of the feedstream or product stream. The TAN is the quantity of base, expressed as milligrams of potassium hydroxide per gram of sample, required to titrate a sample to a specified end point, as measured by ASTM method D-664. A more acidic hydrocarbon product stream can have a detrimental effect on processing equipment, etc. because of its corrosive nature.



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Thus, one embodiment of the instant invention involves separately contacting the first and second hydrocarbon product streams, prior to hydroprocessing, with an effective amount of an acid-reducing material selected from caustic and water, preferably water. By an effective amount of material, it is meant that amount of material that reduces the TAN of the hydrocarbon product stream. The hydrocarbon product streams are contacted with the acid reducing material under effective conditions. By effective conditions, it is meant those conditions, that when selected, allow for the reduction of the TAN of the hydrocarbon product stream. Preferably the effective amount of acid reducing material and the effective conditions are selected such that the TAN of the hydrocarbon product streams are equal that of their respective hydrocarbon feedstreams. More preferably the effective amount of the acid reducing material and the effective conditions are selected such that the TAN of the hydrocarbon product streams is lower than that of their respective hydrocarbon feedstreams

[0041] In one embodiment, the hydrocarbon product streams will also typically have a sulfur concentration lower than that of their corresponding hydrocarbon feedstreams. Thus, the contacting of the hydrocarbon feedstreams in the first and second contacting stages with the sulfuric acid solutions also reduces the sulfur content of the respective hydrocarbon product streams. However, it is desirable to minimize the reduction of sulfur to minimize yield losses. Typically the first and second hydrocarbon product stream will have a sulfur content about 0.1 to about 25% lower than their respective hydrocarbon feedstreams, preferably about 0.1 to about 5% lower.

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[0042] The above description is directed to several embodiments of the present invention. Although the above description is directed at the use of only two contacting stages, the inventors hereof contemplate the use of more than two contacting stages. For example, the second stage sulfuric acid solution can be cascaded to a third contacting stage and contacted with a third hydrocarbon stream having a nitrogen concentration lower than that of the second hydrocarbon feedstream, etc. The limiting factor on the number of contacting stages shall typically be the strength of the sulfuric acid solution because it must still have sufficient strength to perform the desired reduction of nitrogen. Thus, those skilled in the art will recognize that other embodiments that are equally effective could be devised for carrying out the spirit of this invention.

[0043] The following examples will illustrate the improved effectiveness of the present invention, but is not meant to limit the present invention in any fashion.

## **EXAMPLES**

### **EXAMPLE 1**

[0044] A 100N lube raffinate having 18 wppm nitrogen and 6350 wppm sulfur was treated with a spent alkylation unit acid solution at a volumetric treat rate of 0.5 vol.%, based on the raffinate. The sulfuric acid had an equivalent sulfuric acid concentration of 96 wt.%

[0045] 40 ml of the raffinate was placed in a 100cc centrifuge tube and warmed in a water bath to 60°C to melt its wax content. 0.2 ml of the spent alkylation acid solution was then added and the centrifuge tube was shaken by hand for 60 seconds and the mixture was then centrifuged at 1500 rpm for 10

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minutes. The raffinate hydrocarbon product was then poured away from the used sulfuric acid solution and analyzed. The nitrogen content was reduced to 1 wppm.

[0046] The used sulfuric acid solution was left in the centrifuge tube and 8.7 grams 10 mls of a diesel boiling range hydrocarbon having 388 wppm nitrogen and 1.79 wt.% sulfur was added to the centrifuge tube containing the used sulfuric acid solution. The centrifuge tube was again shaken by hand for 60 seconds and centrifuged at 1500 rpm for 10 minutes. The diesel hydrocarbon product was then poured away from the used sulfuric acid solution, weighed and analyzed. The diesel hydrocarbon product weighed 8.6 grams, which represents recovering 99% of the weight of the diesel added to the sulfuric acid solution. The acid byproduct product in this case was a fluid at room temperature.

[0047] The treated diesel was washed with water and analyzed by ANTEK for nitrogen and sulfur. The diesel product contained 95 wppm N and 1.58 wt.% sulfur.

**EXAMPLE 2 (COMPARATIVE EXAMPLE):**

[0048] 40 ml of the same diesel hydrocarbon as in example 1 was placed in a 100cc centrifuge tube and 0.8 ml of the spent alkylation acid solution was then added. The centrifuge tube was shaken by hand for 60 seconds and centrifuged at 1500 rpm for 10 minutes. The diesel hydrocarbon product was then poured away from the used sulfuric acid solution, weighed and analyzed. The acid byproduct was a tarry, viscous fluid at room temperature. The treated diesel was washed with water and analyzed by ANTEK for nitrogen and sulfur.

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The diesel product contained 158 wppm N and 1.58 wt.% sulfur. A total of 96 wt% of diesel product was recovered, representing a 4 wt% yield loss to the acid.

[0049] While not wishing to be limited by theory, the inventors hereof believe that by pre-equilibrating the acid with heavy molecules by treating the 100N raffinate, the used sulfuric acid solution has a reduced capacity to remove similar molecules from the diesel by simple equilibration.